

Thermodynamical Consistency of Excluded Volume Hadron Gas Models

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Abstract

The new excluded volume hadron gas model by Singh et al. [1–7] is critically discussed. We demonstrate that in this model the results obtained from relations between thermodynamical quantities disagree with the corresponding results obtained by statistical ensemble averaging. Thus, the model does not satisfy the requirements of thermodynamical consistency.

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I. INTRODUCTION

In order to take into account the effect of particle repulsion at short distances the excluded volume procedure was proposed by van der Waals in 1873. In a system with a fixed number of particles N this procedure corresponds to a substitution of the system volume V by the available volume $V - vN$, where v is a proper particle volume. This proposal was further supported by the calculations within statistical mechanics for a system of hard spheres of radius r at small particle number densities. In this case, v equals the particle hard-core volume $4\pi r^3/3$ multiplied by a factor of four. The excluded volume procedure leads to the equation of state:

$$p(V - vN) = NT, \quad (1)$$

or equivalently

$$p(1 - vn) = nT, \quad (2)$$

instead of the ideal gas relation

$$p_{id} = n_{id} T. \quad (3)$$

In the above equations, p and T are pressure and temperature, respectively, and $n = N/V$ is particle number density.

The hadron gas is a system with conserved charges (baryonic number, electric charge, strangeness), but with a variable number of particles. Thus, for the hadron gas the excluded volume procedure (1) with a variable number of particles is needed. The first step is to develop the excluded volume procedure in the grand canonical ensemble (GCE), as in the GCE a summation over number of particles is performed.¹ This step appeared to be not trivial. The correct excluded volume procedure in the system with a variable number of particles was first introduced in Ref. [8]. Several other proposals [9–11] do not satisfy the thermodynamical relations.

Recently, the new excluded volume model has been developed by Singh et al. [1–7] (we refer to it as NEVM). In the grand canonical partition function the authors substitute the system

¹ The excluded volume procedure with a variable number of particles is also needed for the hadron gas in the canonical and micro-canonical ensembles. For these ensembles the conserved charges are exactly fixed, but the number of particles still remains a variable quantity.

volume V by the available volume $V(1 - \sum_j v_j n_j)$, where sum is taken over different particle species, n_j is the j -th particle number density, and v_j is the proper volume parameter of the j -th hadron. Contrary to the statements in Refs. [1–7] this procedure is not thermodynamically consistent. In order to prove this we consider the simplest example of the system with a single particle type obeying Boltzmann statistics.

II. THERMODYNAMICAL CONSISTENCY

As a first step let us discuss general requirements of thermodynamical consistency. In GCE the partition function is given as the sum over states i :

$$Z(V, T, \mu) = \sum_i \exp \left(\frac{\mu N_i - E_i}{T} \right), \quad (4)$$

where N_i and E_i are the number of particles and system energy in i -state, T and μ are the system temperature and chemical potential, respectively. The system pressure is calculated as

$$p \equiv \frac{T}{V} \ln Z(V, T, \mu), \quad (5)$$

whereas particle number density n and energy density ε are found using the thermodynamical relations

$$n(T, \mu) = \frac{\partial p}{\partial \mu}, \quad (6)$$

$$\varepsilon(T, \mu) = T \frac{\partial p}{\partial T} + \mu \frac{\partial p}{\partial \mu} - p. \quad (7)$$

Thus, thermodynamical average quantities for the number of particles and system energy are equal to:

$$\overline{N} = V n(T, \mu), \quad (8)$$

$$\overline{E} = V \varepsilon(T, \mu). \quad (9)$$

In order to fulfil the thermodynamical relations (6) and (7) a correct structure of the partition function as a sum over the system states i is required. The quantities T and μ may only enter $Z(V, T, \mu)$ in the very definite way, i.e., only as given by Eq. (4). Under these conditions the

GCE statistical averages

$$\langle N \rangle = \frac{1}{Z(V, T, \mu)} \sum_i N_i \exp \left(\frac{\mu N_i - E_i}{T} \right), \quad (10)$$

$$\langle E \rangle = \frac{1}{Z(V, T, \mu)} \sum_i E_i \exp \left(\frac{\mu N_i - E_i}{T} \right), \quad (11)$$

can be calculated using T - and μ -derivatives as

$$\langle N \rangle = \frac{1}{Z(V, T, \mu)} \sum_i T \frac{\partial}{\partial \mu} \exp \left(\frac{\mu N_i - E_i}{T} \right) = T \frac{\partial}{\partial \mu} \ln Z(V, T, \mu) = V \frac{\partial p}{\partial \mu}, \quad (12)$$

$$\begin{aligned} \langle E \rangle &= \frac{1}{Z(V, T, \mu)} \sum_i \left(T^2 \frac{\partial}{\partial T} + T \mu \frac{\partial}{\partial \mu} \right) \exp \left(\frac{\mu N_i - E_i}{T} \right) \\ &= \left(T^2 \frac{\partial}{\partial T} + T \mu \frac{\partial}{\partial \mu} \right) \ln Z(V, T, \mu) = V \left[T \frac{\partial p}{\partial T} + \mu \frac{\partial p}{\partial \mu} - p \right], \end{aligned} \quad (13)$$

in agreement with thermodynamical relations (6) and (7), i.e., the thermodynamical averages, \overline{N} (8) and \overline{E} (9), and statistical averages $\langle N \rangle$ (10) and $\langle E \rangle$ (11), are equal to each other:

$$\langle N \rangle = \overline{N}, \quad \langle E \rangle = \overline{E}. \quad (14)$$

III. NEW EXCLUDED VOLUME MODEL [1–7]

NEVM [1–7] assumes the following expression for the GCE partition function

$$\begin{aligned} Z(V, T, \mu) &= \sum_{N=0}^{\infty} \exp \left(\frac{\mu N}{T} \right) Z(V, T, N) = \sum_{N=0}^{\infty} \exp \left(\frac{\mu N}{T} \right) \frac{(V - v\overline{N})^N}{N!} z^N \\ &= \exp \left[\exp(\mu/T) (V - v\overline{N}) z \right], \end{aligned} \quad (15)$$

where

$$z(T) = \frac{g}{2\pi^2} \int_0^{\infty} k^2 dk \exp \left[- \frac{(k^2 + m^2)^{1/2}}{T} \right] \quad (16)$$

is the so-called one-particle partition function. In Eq. (16), m and g are the particle mass and the degeneracy factor, respectively. The quantity \overline{N} in Eq. (15) is an average number of particles calculated with Eq. (8). From Eq. (15) one finds the pressure:

$$p \equiv \frac{T}{V} \ln Z(V, T, \mu) = T \exp(\mu/T) (1 - vn) z = (1 - vn) p_{id}. \quad (17)$$

Note that

$$n_{id}(T, \mu) = \exp(\mu/T) z(T) \quad (18)$$

is the particle number density in the ideal gas (i.e., at $v = 0$), and the ideal gas pressure p_{id} is given by Eq. (3). The particle number density $n(T, \mu)$ is calculated in NEVM [1–7] using the thermodynamical relation (6), which together with Eq. (17) yields:

$$n = \left(1 - vn - vT \frac{\partial n}{\partial \mu} \right) n_{id} . \quad (19)$$

The pressure (17) and particle number density (19) in NEVM are connected by the thermodynamical relation (6). Note, however, that in NEVM relation (17) which connects p and n is different from that given by Eq. (2). The thermodynamical relations (6) and (7) do not correspond in NEVM to correct statistical averaging of the number of particles (10) and system energy (11). The canonical partition function in (15) reads:

$$Z(V, T, N) = \frac{(V - v\overline{N})^N z^N}{N!} , \quad (20)$$

with \overline{N} given by Eq. (8). A presence of \overline{N} , which is a function of T and μ , in the partition function (15) destroys the correct structure (4) of the GCE partition function, thus, it leads to a violation of the thermodynamical consistency. The thermodynamical relations (6) and (7) do not correspond to correct statistical averaging in NEVM, i.e.,

$$\langle N \rangle \neq \overline{N} , \quad \langle E \rangle \neq \overline{E} . \quad (21)$$

Therefore, the thermodynamical relations (6) and (7) used in NEVM to calculate particle number density and energy density are in contradiction with statistical averages (10) and (11). This is because a presence of $\overline{N} = Vn(T, \mu)$ in the partition function (15), which leads to the redundant terms in Eqs. (12) and (13). These incorrect terms come from the derivatives of \overline{N} in respect to μ in (12) and in respect to T in (13).

IV. EXCLUDED VOLUME HADRON GAS MODEL [8]

The excluded volume model [8] is based on the equation for the grand canonical partition function:

$$Z(V, T, \mu) = \sum_{N=0}^{\infty} \exp\left(\frac{\mu N}{T}\right) \frac{(V - vN)^N}{N!} \theta(V - vN) z^N . \quad (22)$$

The form of the available volume $(V - vN)$ with the theta function $\theta(V - vN)$ instead of $V - v\overline{N}$ in (15) causes some technical problems for the summation in (22) over N . On the other hand,

just this form of the available volume makes the formulation thermodynamically consistent. It is easy to see that the thermodynamical relations (6) and (7) are in agreement with statistical averaging (10) and (11) for the partition function (22). In calculations one uses the Laplace transform of (22):

$$\begin{aligned}\hat{Z}(s, T, \mu) &= \int_0^\infty dV \exp(Vs) Z(V, T, \mu) = \sum_{N=0}^\infty \frac{[z \exp(\mu/T)]^N}{N!} \int_{vN}^\infty dV (V - vN)^N \exp(-sV) \\ &= \frac{1}{s} \sum_{N=0}^\infty \left[\frac{\exp(-v s) z \exp(\mu/T)}{s} \right]^N = \left[s - \exp(-vs) n_{id}(T, \mu) \right]^{-1}.\end{aligned}\quad (23)$$

The system pressure in the thermodynamic limit can be then found from the farthest-right singularity s^* of \hat{Z} (23) as a function of s :

$$p(T, \mu) = \lim_{V \rightarrow \infty} \frac{T}{V} \ln Z(V, T, \mu) = T s^*(T, \mu). \quad (24)$$

The singularity s^* is the pole singularity for (23), which leads to the transcendental equation for the pressure:

$$p = \exp(-vp/T) p_{id}. \quad (25)$$

Using the thermodynamical relation (6) one finds

$$n = \frac{n_{id} \exp(-vp/T)}{1 + v n_{id} \exp(-vp/T)}. \quad (26)$$

Note that Eqs. (25-26) are different from Eqs. (17) and (19) of NEVM [1–7]. Combining Eqs. (25-26) and using the relation $p_{id} = T n_{id}$ one obtains after simple algebra which coincides with Eq. (2).

V. CLOSING REMARKS

There are great difficulties in a formulation of statistical theory of hadrons from the first principles. Models in this field are of a phenomenological origin. An important constrain in model formulation is the requirement of thermodynamical consistency. The thermodynamical consistency can be violated in different ways. Two examples are illustrated by considering the excluded volume model. In the first example, the inconsistency appears when one substitutes the system volume by the available volume in all ideal gas thermodynamical functions. This was done, e.g., in Refs. [9–11]. The available volume is a function of temperature and chemical

potential, thus, the redundant terms appear, and the thermodynamical relations (6,7) are not fulfilled after this substitution. The second example of the inconsistency can be seen in the new excluded volume model of Refs. [1–7]. In this model one substitutes the system volume by the available volume in the GCE partition function. Then the available volume is used to calculate the pressure function only. Other thermodynamical functions are calculated using the thermodynamical relations (6,7). However, the available volume being a function of T and μ , destroys the correct structure of the GCE partition function. This leads to a violation of the thermodynamical consistency, i.e., results obtained from thermodynamical relations (6,7) and from statistical averaging are different.

Several comments concerning the excluded volume model [8] should be added. The (effective) proper volume v used in this model is a model parameter. For a “rigid” balls it is a ball volume multiplied by a factor of 4. For “soft” hadrons this factor will have a value between 1 and 4. However, in most cases the proper volume v is treated as a free parameter fitted to data.

A simplest case of a gas of identical particles was considered in the above presentation for didactic reasons. The consistent formulation of the excluded volume hadron gas model can be easily extended to many particle species with different proper volume parameters (see, for example, Ref. [12]).

The effect of relativistic contraction is expected to be small in the hadron gas. This is because the hadron gas temperature is significantly smaller than almost all hadron masses and thus hadrons are non-relativistic. This is not true for pions, their masses are comparable to temperature. But a predominant majority of pions comes from resonance decays, and resonance masses are again significantly larger than the gas temperature. Most important relativistic effect in the hadron gas model is a variable number of hadrons. But this feature is exactly the main point of the consistent formulation (22-26) of the excluded volume hadron gas model.

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